PB-240 961

STATE-OF-THE-ART FOR THE INORGANIC CHEMICALS INDUSTRY

INDUSTRIAL INORGANIC GASES

ILLINOIS INSTITUTE OF TECHNOLOGY

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

MARCH 1975

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This report has been reviewed by the Office of Research and Development. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ia

SELECTED WATER RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

3. Accession No.
W PB-240-961

4. Title
State-of-the-Art For The Inorganic Chemicals Industry: Industrial Inorganic Gases

7. Author(s)
James W. Patterson, Ph.D.
Roger A. Minear, Ph.D.

9. Organization
Department of Environmental Engineering
Illinois Institute of Technology
Chicago, Ill. 60616

10. Project No.
PE 1BB036 R/T 21 AZQ29

11. Contract/Grant No.
R-800857

15. Supplementary Notes
Environmental Protection Agency report number, EPA-600/2-74-009c, March 1975

16. Abstract
A literature and field study of the inorganic gas industry revealed that the industry is dominated by (1) air separation plants producing argon, nitrogen and/or oxygen, (2) hydrogen plants and (3) carbon dioxide plants. The major effluent of the industry is cooling water, which may be contaminated with raw product condensates, oil and grease, and water supply and cooling water treatment chemicals. Spent scrubber solutions from product purification may also constitute a significant waste, although newer production technology eliminates this aspect, as well as oil and grease.

17a. Descriptors

17b. Identifiers

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
US Department of Commerce
Springfield, VA. 22151

PRICES SUBJECT TO CHANGE

17c. COWRR Field & Group

18. Availability

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor

Institution

EPA-600/2-74-009c
March 1975

STATE-OF-THE-ART FOR THE INORGANIC CHEMICALS INDUSTRY: INDUSTRIAL INORGANIC GASES

BY

James W. Patterson, Ph.D.

and

Roger A. Minear, Ph.D.

Project R-800857
Program Element 1BB036
ROAP 21 AZQ Task 029

Project Officers

Mr. Elwood E. Martin
Office of Water and Hazardous Materials Programs
Washington, D. C. 20460

and

Mr. Richard B. Tabakin
Industrial Pollution Control Branch
Industrial Waste Treatment Research Laboratory
Edison, New Jersey 08817

for the

Office of Research and Development
United States Environmental Protection Agency
Washington, D. C. 20460

ABSTRACT

A literature and field study of the inorganic gas industry revealed that the industry is dominated by (1) air separation plants producing argon, nitrogen and/or oxygen, (2) hydrogen plants and (3) carbon dioxide plants. The major effluent of the industry is cooling water, which may be contaminated with raw product condensates, oil and grease, and water supply and cooling water treatment chemicals. Spent scrubber solutions from product purification may also constitute a significant waste, although newer production technology eliminates this aspect, as well as oil and grease.

CONTENTS

Section		Page
I.	Conclusions	1
II.	Recommendations	3
III.	Introduction	5
IV.	Study Methodology	9
V.	Industry Categorization	11
VI.	Waste Characterization	19
VII.	Control and Treatment Technology	47
VIII.	Acknowledgements	49
IX.	References	50
X.	Appendix	53

Preceding page blank

FIGURES

		Page
1.	Schematic of Air Separation Process	12
2.	Comparison of Production to Water Use	23
3.	Distribution of Plant Production	25
4.	Distribution of Water Use	26
5.	Distribution of Air Separation Plant Production	27
6.	Distribution of Air Separation Plant Water Use	28
7.	Distribution of Waste Volumes	34

TABLES

		Page
1.	Summary of Gas Production Sites	7
2.	Summary of Major Gas Producers	8
3.	Summary of Production Lines Visited	10
4.	Source of Raw Carbon Dioxide Gas	17
5.	Summary of Water Use	21
6.	Waste Volume per Ton of Product	32
7.	Pollutant Concentration Factors	36
8.	BOD and COD Concentrations	38
9.	Mass Discharge of BOD and COD	39
10.	Discharge of Chromium	41
11.	Discharge of Zinc	42
12.	Discharge of Oil and Grease	43
13.	Summary of Temperature Data	45

I. CONCLUSIONS

The industrial inorganic gas industry consists of a large number of facilities primarily involved in the production of argon, carbon dioxide, hydrogen, nitrogen and oxygen. The industry may be classified into three segments; air separation plants which produce argon, nitrogen and/or oxygen by separation of air into the product components, hydrogen plants which utilize various raw materials and methods of hydrogen generation, and carbon dioxide plants utilizing combustion, fermentation, carbonate calcining or ammonia manufacture by-products as raw material. Plants of the gas industry are typically located adjacent to either their source of supply of raw material, or for customer convenience.

Wastewaters of the industry primarily result from cooling water use, and contain in addition pollutants associated with processing and product purification. The range of cooling water use is wide, and the volume dependent upon the extent of cooling water recycle. The nature of the wastewater is dictated by additives to recycled cooling water, the use of lubricated versus non-lubricated compressors, the source of the raw materials, and the product purification techniques used. Typical wastewater constituents include chromium and zinc from cooling water treatment, BOD from process gas organic condensates, oil and grease from lubricated compressors, and exhausted gas scrubber solutions employed for product purification. In general, newer technology eliminates discharges of oil and grease, as well as spent scrubber solution. Substitution of other cooling water treatment chemicals for chromium and zinc compounds is increasingly employed. Use of these and similar in-plant modifications can significantly reduce or eliminate many of the more critical pollutants of the industry.

Remaining problems are primarily associated with thermal discharge and total dissolved solids relating to blowdown from cooling systems, as well as process condensate from carbon dioxide plants. In these facilities the raw material may contain significant quantities of condensible organics which, upon product purification, constitute a major waste discharge.

II. RECOMMENDATIONS

Current wastewater problems in the inorganic gas industry may be categorized as:

1. Those associated with use of older technology, including use of scrubber solutions, and oil and grease leakage from lubricated compressor.
2. Pollutants resulting from compounds added to recycle cooling water systems, particularly chromium and zinc compounds.
3. Raw material condensates generated in the process of product purification.

Of these, the first category can be eliminated by use of newer technology, which includes non-lubricated compressors and thermally regenerated purification units. However, there are many plants which incorporate the older processes, and only the most rudimentary treatment techniques are employed in those plants which do attempt to treat their wastewaters. These plants require small scale, economical and reliable treatment processes for their wastes.

Insofar as the second category, additives to cooling water systems, chromium and zinc compounds should be substituted by other commercial corrosion control and biocide chemicals. This has, in fact, taken place in a significant number of gas plants, thereby eliminating the problem of heavy metal discharge.

The problem of raw material condensates appears to be particularly critical in the carbon dioxide segment of the industry, dependent upon the type of raw material used. One carbon dioxide plant receiving raw gas from an adjacent petrochemical plant, reported one pound of condensate waste per pound of CO_2 product. Such wastes are complex and rich in organics, and represent a significant pollution potential from carbon dioxide facilities. Limited information was available from this study to substantiate this concern, and expansion of the data base for carbon dioxide facilities is recommended. Additionally, many of the CO_2 plants

Preceding page blank

received by-product from ammonia production facilities, and the potential for condensate pollution from this source is also high.

This report does not discuss the molecular-sieve-type processes developed and used by the Linde Division of Union Carbide for the production and/or purification of oxygen and nitrogen. These resin technologies are gaining increased attention in some oxygen and nitrogen consuming industries. It is recommended that a study be performed to compare the waste generation and energy requirements for the cryogenic versus molecular-sieve processes.

III. INTRODUCTION

The specific industries examined as the basis for this report were those producing the inorganic industrial gases (SIC 2813), Argon, Carbon Dioxide, Hydrogen, Nitrogen and Oxygen. Neon in crude form is occasionally a by-product of the air separation process which yields argon, nitrogen and oxygen, and is mentioned in that respect only. Helium, which is a noncondensible gas in normal air separation processes, was not included in the study.

General Description of the Industry

Although a given industrial plant may engage in more than one production process, the industry has been divided into 3 specific categories, each of which has varying technology. These categories are (1) Air Separation or Rectification, which encompasses production of liquid or gaseous argon, nitrogen and oxygen (A/N/O), and occasionally crude neon product, (2) hydrogen gas or liquid production and, (3) carbon dioxide liquid or solid production. Specific variations in the generation of final product within each of these categories is described in Chapter V.

The physical form of the product and its purity is variable, and dependent upon the particular market requirement. Many plants in the air separation category serve specific industrial sites, and tailor their process to the needs of that industry. Notable in this respect are air separation plants designed to produce only gaseous oxygen for pipeline delivery to adjacent steel mills or iron ore processing operations (taconite ore enrichment). When plant location is not remote, only a portion of the product is sold via pipeline, and production is geared to providing bulk liquid and gaseous argon and nitrogen, in addition to oxygen, for direct bulk sale in tank trucks, or individual cylinders. Many combinations of marketing procedures exist, and for a given plant production for a given category may vary with time, with attendant variation in plant operation procedures.

Many plants, notably air separation plants and those producing hydrogen, are captive industries within a larger manufacturing complex. Frequently, this results in water use and wastewater treatment data being undifferentiable from the total plant flow and waste character data.

A summary of production sites in the ten regions of the Environmental Protection Agency is given in Table 1. Of the total 472 plants, 308 or 65.2% can be attributed to 8 major producers. These are summarized in Table 2 by manufacturer and EPA region. Production capacities range from a few tons/day of combined product gases and liquids to ten thousand or more tons/day. Production data were available for less than half of the total reported plants.

Distribution of the inorganic industrial gas manufacturing plants is coincident with the major industrial regions of the country, as indicated by the high density of production sites in EPA regions III, IV, V, VI and XI. Principally, the major steel, petroleum and fertilizer manufacturing areas either use large quantities of the various gases, or produce by-product raw material which is sold to the industry for gas manufacture.

Table 1. Summary of Industrial Gases (Inorganic) Production Sites*

Product	EPA Region										Total
	I	II	III	IV	V	VI	VII	VIII	IX	X	
Carbon Dioxide	2	12	14	18	26	15	13	4	13	7	124
Hydrogen	4	16	20	23	36	28	8	3	29	4	171
Argon/Nitrogen/ Oxygen	4	11	35	20	38	27	3	6	28	5	177
Totals	10	39	69	61	100	70	24	13	70	16	472
% of Total	2.1	8.3	14.6	12.9	21.2	14.8	5.1	2.8	14.8	3.4	100.0

* Data from The Directory of Chemical Producers (Stanford Research Institute, 1972)

Table 2. Summary of Major Producers* of Industrial Gases (Inorganic)

Producer	Major Products	Region I	II	III	IV	V	VI	VII	VIII	IX	X	Total
1. Airco, Inc.	A/N/O CO_2, H_2	3	4	6	4	8	1	2	0	6	1	35
2. Air Products and Chem., Inc.	A/N/O H_2	0	6	13	6	11	7	1	0	4	0	48
3. Big Three Industries	A/N/O H_2	0	0	0	3	0	10	0	0	0	1	14
4. Burdett Oxygen Company	A/N/O H_2	0	1	3	0	3	0	0	0	0	0	7
5. Chemetron Corp. and Cardox Div.	A/N/O H_2, CO_2	0	3	8	3	10	5	1	3	1	1	35
6. Houston Nat. Gas	A/N/O CO_2, H_2	3	9	6	12	16	10	5	1	4	2	68
7. Process Plants	CO_2	0	0	2	1	1	3	0	0	0	0	7
8. Union Carbide	A/N/O CO_2, H_2	5	7	20	6	23	11	5	4	12	1	94
Totals		11	30	58	35	72	47	14	8	27	6	308

* Producers with more than five production sites.
Data from The Directory of Chemical Producers (Stanford Research Institute , 1972)

IV. STUDY METHODOLOGY

Characterization of the subject industry was accomplished by (1) use of published data describing the extent and distribution of industrial sites and the principal manufacturing processes employed, (2) selected site visits to a small but representative cross section of manufacturing locations and (3) review of existing RAPP permit applications on file within the EPA regional offices. Frequently, this latter source provided insufficient information, particularly regarding product identification and/or production yields, to allow utilization of all permit applications in summarizing general waste character.

Little specific information regarding waste treatment facilities and their efficiency, cost, and operational problems was available either from plants visited or from permit application files. Because of the nature of the basic manufacturing processes and the individual variations, however, the industry waste problems can be identified and treatment solutions can be projected directly to known unit operations and/or process modifications. Existing literature, and experience demonstrated through plant visitations, has been utilized to accomplish these basic goals of the study.

A total of ten separate plants were visited, representing 22 separate production lines (exclusive of crude argon rectification and deoxygenation). Table 3 delineates these production lines.

All data accumulated from these plant visits were provided by plant or corporation personnel from their files. No independent sampling and analysis was undertaken.

Table 3. Summary of Separate Production Lines Existing at Plants Visited

Process Line	Number
Air Separation	
A/N/O	10
N/O	2
O_2 only	2
N_2 only	2
Hydrogen	5
CO_2	1

V. INDUSTRY CATEGORIZATION

This section presents a description of the basic production technologies employed in each of the 3 major subgroupings of the industry; air separation, hydrogen production, and carbon dioxide production. In general, this division is logical as each of these product lines is distinct with a few exceptions, which will be pointed out where appropriate.

Within each of these subgroups there are several variations relating to the actual manufacturing process used, manner in which a particular physical or chemical operation is effected, design of equipment accomplishing a specific operation, and entry level of the product raw material into the process. In some instances, these variations are the result of advancing technology within the industry, and impact strongly on the quantity and character of process waste water. The air separation process best exemplifies this change in production technology.

Air Separation

The air separation process fractionates atmospheric air into its component gases, at varying levels of purity depending upon need, by fractional distillation and condensation. Normally, the products are oxygen and nitrogen in both liquid and gaseous states. Crude argon and neon may be separate by-products of the basic separation process, which are then individually subjected to further purification. Argon rectification and deoxygenation are generally closely connected with the basic air separation system, frequently within the same cold box system. Neon is noncondensible and recovered as neon enriched nitrogen, which is subjected to separate purification. Of 16 air separation lines visited, only one collected crude neon. This plant shipped it off-site for purification.

Conceptually, the sequence of operations in all air separation plants is identical. These operations are represented schematically in Figure 1. The filtration step is generally a simple dry inlet filter to remove particulate matter, prior to the compression step. Depending

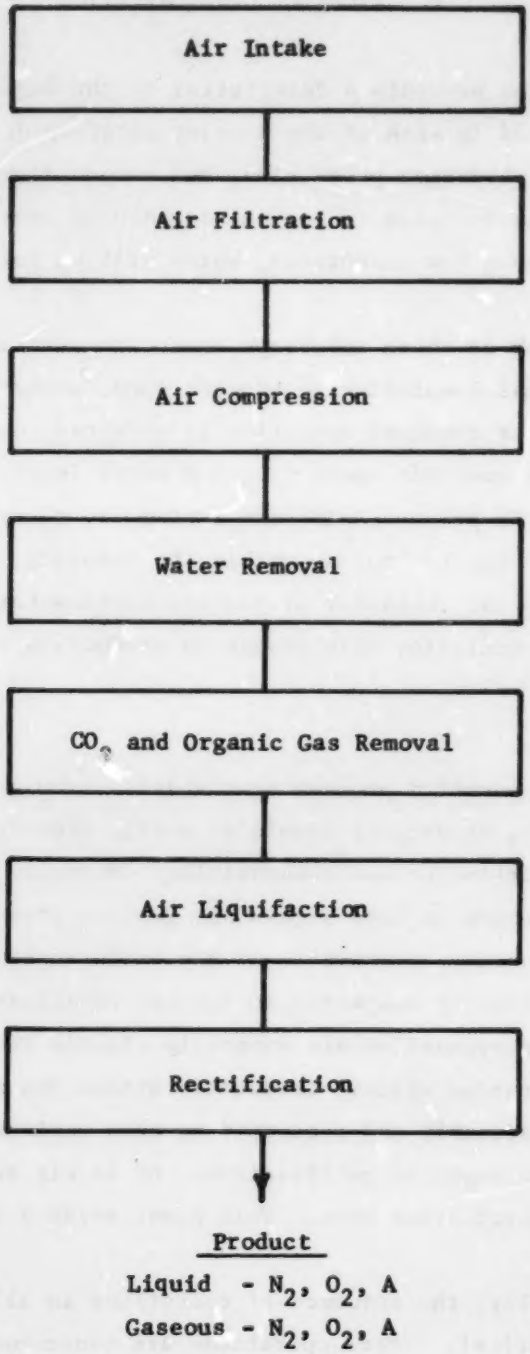

Figure 1. Sequence of operations in the Air Separation Process

upon the overall process design, the air may be compressed from as little as 60-80 psig to as high as 2700 psig. Intermediate pressures of 80 to 100 psig were more common in those plants visited. The compression is accomplished in stages with cooling after each stage, during which moisture in the air condenses and is discharged. Generally cooling is provided by jacketed noncontact systems, although a few plants employed direct contact cooling after the final compression stage.

Depending upon the nature of the compression unit, the condensates may be essentially pure water or a significant contaminant stream. Most recently constructed plants employ axial flow turbine or centrifugal compressors, which are nonlubricated. Although some nonlubricated piston compressors were encountered, most reciprocating compressors were lubricated and the condensate discharge constitutes an oily waste. Compressors were driven by a variety of systems; electric motors powered by commercial electricity, electric motors powered by steam driven generators on-site, steam driven turbines, and gas fired turbines with steam assist turbines utilizing the high temperature exit gas to fire waste heat boilers. Occasionally, two multistage compressors were used, with a cleanup step between the compressors.

Residual water, carbon dioxide and contaminant organic gases are removed from the pressurized air stream prior to expansion and liquifaction. Older technology effected CO_2 removal by direct contact with strong caustic solution (10% NaOH). Only two plants were encountered which used this process and it is generally acknowledge to be out of date. Modern plants accomplish cleanup by passing the gas stream through some combination of molecular sieves, alumina columns, silica gel traps or reversing heat exchangers. In the latter case, CO_2, water and organic gases are removed as solids or liquids in the heat exchanger in counter current flow with product nitrogen and oxygen. The latter are at very low temperatures. All of these cleanup units are thermally regenerated off stream, and vent the contaminants to the atmosphere.

At this point, the compressed air is liquified and cooled by heat exchanger systems and various expansion techniques. Cold product gases

generally supply the cooling, although occasionally auxillary nitrogen and freon systems are used. Expansion cooling is commonly achieved by turbine expanders although piston expansion engines are employed to a limited extent. Depending upon the exact process some combination of expansion processes may be used in conjunction with partial by-pass of the expansion system.

The liquified or partially liquified air passes into separation towers, generally at 70-90 psig. Depending upon the desired product, the rectification or separation section (called the cold box) may consist of only a high pressure column, or both a high pressure and a low pressure column. For argon purification a third column is employed. Gas enters into the low pressure column at a pressure of 5-9 psig. Product take off points and exact entry and return points are dictated by product purity, quantity and balance between liquid and gaseous forms of the individual products desired. There is no wastewater effluent associated with the cold box system.

Product is fed back through the heat exchanger system for cooling incoming air, as may be waste gases prior to atmospheric venting. Liquid product is sent to bulk storage. Gaseous product is usually at low pressure and subsequently undergoes compression prior to bulk storage, bottling or direct pipeline distribution to neighboring industrial operations. Product gas at roughly 4 psig is compressed to 200 to 3000 psig, using nonlubricated centrifugal or piston multistage compressors with cooling between each of the stages. Generally closed water jacket cooling is used, although some operations employ freon cooling units.

Argon product emanating from the separate argon rectification tower contains roughly 2% oxygen and must undergo additional processing. Deoxygenation is accomplished in a catalytic bed with ammonia and/or hydrogen. Resultant water and dissolved oxides of nitrogen are condensed and discharged. This may yield a wastewater high in nitrate and nitrite. Argon is liquified by liquid nitrogen cooling, and residual nitrogen gas impurity is vented prior to pumping to bulk storage.

Hydrogen

Hydrogen production is accomplished primarily by steam-hydrocarbon reforming (natural gas or propane). Catalytic cracking of ammonia, or high purity hydrogen production by electrolysis of aqueous alkaline or brine solutions are lesser used methods. The latter process also produces oxygen. Each of these three processes was encountered during site visits. Other processes have been mentioned in the literature, eg. steam - iron process, thermal dissociation of natural gas to produce carbon black, fermentation and others in which hydrogen is a by-product of other manufacturing processes. These processes are most commonly employed by industries other then the gas industry. The by-product hydrogen may be used on site or piped to adjacent independent facilities for further processing for marketing.

The steam-hydrocarbon reforming process involves passing propane (desulfurized if necessary) or natural gas (CH_4) and steam at roughly 100 psig into a heated (1500°F) reformer furnace. The reformer is usually a gas fired catalytic bed of nickel, contained in alloy tubes within a furnace. Products from this unit are H_2, CO, CO_2 and water. Carbon monoxide is converted to CO_2 by a second catalytic converter of cupric oxide, possibly with the addition of more steam and production of additional hydrogen gas. The hot gases are cooled either by a water jacket system or heat exchanger employing downstream product, prior to CO_2 removal. Condensate is discharged from the cooling systems. A second stage CO converter may be present, particularly in a propane system.

Carbon dioxide removal is accomplished by scrubbing with a monoethanolamine (MEA) solution. Purified hydrogen is further cooled (water jacket) and dried with an alumina column. The product may be stored and shipped in bulk, or piped directly to near-by customers. Monoethanolamine is regenerated in a heated stripping tower, venting CO_2 to the atmosphere and condensing MEA, which is cooled by water jacket cooling and returned to the scrubber. Water condensate is discharge from the unit.

Other hydrocarbon processes are used, but were not encountered in

this study. These employ partial oxidation by mixing 95% oxygen with preheated hydrocarbons (up to fuel oil) in a catalytic bed. A mixture of hydrogen (34%), carbon monoxide (16%), carbon dioxide (2%), water vapor (2%), methane (1%) and nitrogen (45%) is produced. Hydrogen production by this method ranks second only to the reforming process.

Ammonia cracking involves vaporizing anhydrous liquid ammonia, heating to 1600-1750°F, and passing over an active catalytic bed. Nitrogen and hydrogen gases are produced in the volume ratio of 1 to 3. Separation of the two gases is then accomplished. One plant visited compressed the product gases and passed them through molecular sieves. Nitrogen is retained and vented upon regeneration. Product hydrogen contains less than 25 ppm nitrogen contaminant. Both the cracking generator and gas compressors are water cooled. Another plant separated nitrogen and hydrogen by differential liquifaction.

Electrolytic hydrogen generation is employed to a limited extent in the industry, and was utilized by only one of the five hydrogen lines visited in this study. The process is relatively simple, with electrolysis of water in electrolytic cells to produce gaseous hydrogen and oxygen. The gas mixture is separated into its two components by differential liquification. High purity products are obtained.

Carbon Dioxide

Product carbon dioxide may be in gas, liquid or solid form. Formation of the solid form incorporates processing the other two physical forms. The starting material is gaseous CO_2 which may be generated on site by burning of carbonaceous material, or received as a by-product of other manufacturing processes either on-site or from nearby manufacturing plants. Flue gases, fermentation and carbonate calcining are the major sources of commercial CO_2 production (1). However, of the 126 industrial producers (exclusive of brewers employing recovery and reuse of CO_2) listed in the Directory of Chemical Producers (Stanford Research Institute, 1972) only 44 reported their raw CO_2 source. The distribution of these sources, shown in Table 4, indicates that ammonia by-product is the major CO_2 source. Representatives of the industry indicate that generation of CO_2 by fuel combustion is declining in the

Table 4. Distribution of Reported Carbon Dioxide Sources

Source	Number of Sources	Percent of Sources
Natural Gas	7	16
Ammonia By-Product	22	50
Fuel Combustion	4	9
Hydrogen By-Product	1	2
Methanol By-Product	1	2
Coke Breeze	1	2
Natural Well	3	7
Sodium Phosphate By-Product	1	2
Flue or Stack Gas	2	5
Lime Kiln By-Product	2	5
	44	100

industry, being replaced by plants utilizing CO_2 by-product, principally from fertilizer plants producing ammonia.

In-coming gas may contain up to 99% CO_2 from fermentation processes and as little as 10% CO_2 from fuel burning or lime kiln sources. Other sources are intermediate in CO_2 concentration. The one plant visited received crude, hot CO_2 gas from an adjacent petrochemical manufacturing operation. The gas yielded 1 lb. condensate (water and organics) per lb. of product CO_2.

Low concentration CO_2 gases employ reversible absorption concentration systems such as ethanolamine or concentrated potassium carbonate solutions. Desorption of concentrated CO_2 is achieved by temperature elevation. Depending upon temperature and moisture content, processing of the CO_2-rich stream may involve passing it through a series of cooling stages to remove water and other condensable substances and possibly an oxidation stage using permanganate solution, dichromate solution or catalytic oxygen oxidizers.

Purified and cooled gas is compressed, cooled, dried and possibly polished by carbon beds and sand filters prior to cooling and liquifaction with liquid ammonia or other cooling systems. Liquid at 290 psig can be collected to storage by bleeding out at slightly reduced pressure (200 psig). Noncondensable gases remaining at this point are vented to the atmosphere. Liquid CO_2 is usually shipped in bulk to local distribution centers for small container filling.

Solid CO_2 is produced by dropping below the triple point pressure by expansion in extruders and rotary expansion devices to produce pellets, or large expansion chambers to produce solid CO_2 snow which is then compressed hydraulically into blocks. Vapor remaining the chamber is returned to the compression stream.

VI. WASTE CHARACTERIZATION

This chapter presents water use data, and describes wastewater sources, volumes and character. Information has been taken from two sources:

(1) Data collected during visits to specific manufacturing sites and

(2) RAPP permit applications on file with EPA.

Specific Water Uses

The primary water use in all three types of facilities is cooling water. For air separation plants, this use is primarily associated with air or product compressor cooling. Most compression operations are multistage. For inlet air, 4 to 5 stages are typical; for product piping or storage, 3 to 6 stages are common. The most frequent practice is to use jacketed cooling systems. Occasionally, direct contact water cooling after the final compression state is employed. A variant on the direct contact configuration, predominantly used in older plants, is to remove carbon dioxide in the compressed gas stream by scrubbing in strong caustic solution. Product compression cooling is always closed jacket, to prevent product contamination.

In hydrogen manufacture, both hydrocarbon reforming and ammonia cracking employ cooling of the hot gases exiting from the high temperature catalytic beds. For hydrocarbon reforming, additional cooling follows the carbon monoxide conversion bed and is also used in the regeneration of monoethanolamine scrubber systems. Product compression is also accompanied by cooling, after the compression stages.

Carbon dioxide, when generated by combustion of hydrocarbons or other low yield processes, must be cooled prior to enrichment in scrubber systems since these systems are reversed (ie. heated) to yield high concentration CO_2 gas. By-product CO_2 may be received at high temperature in admixture with condensible contaminants, in which case the cooling process also serves as a purification step. Purification and

liquifaction of the CO_2 involves compression, and requires cooling at various stages of processing. Most of the cooling steps utilize water cooling. Air and liquid ammonia or freon cooling systems are also employed.

Boiler systems can represent significant water use, but the magnitude of this use is highly variable. The most significant use of boiler systems in air separation plants is when compressors are steam driven or when electric power is generated on-site with a steam powered generator. One instance was encountered where the primary compressor power source was a gas fired turbine. High temperature exit gases in turn fired waste heat boilers, thereby generating steam to drive assist turbine compressors. Generally, boiler systems are present primarily for plant heating and as stand-by units to vaporize backup liquid product storage reserves for pipeline customers. Units are also available to provide rapid thawing of the process units upon plant shut down. For hydrogen production by hydrocarbon reforming, high pressure steam is one of the starting raw materials. This steam is produced on-site. Water use in boiler systems depends upon the steam requirement, and whether condensate return systems are employed.

Miscellaneous other water uses are generally small in comparison to cooling and boiler systems. Among those encountered are:

Scrubber systems
General plant wash down
Spray systems used during bottle or tank filling
Sanitary systems

Water Use Volume

Total water use would be expected to reflect the size or production level of the individual manufacturing facility, and the nature of its products. This would be reflected in a rather narrow range of values upon normalizing water use to a "volume per unit of product" basis. That this is not manifested is demonstrated in Table 5 and Figure 2, where data are presented for 40 plants located throughout the United States. Extremely high water use rates are directly attributable to

Table 5. Water Use Summary for Industrial Inorganic Gas Facilities

Product	Production, T/day	Water Use, MGD	Water Use, gal/ton Product
A/N/O	27	.0235	870
O_2	65	.00095	15
N/O	175	.0436 to .0570	247-329
N/O	180	.21	1,167
N/O	184	.0801	435
N/O	184	.047	255
N/O	270 (O_2)	.09	333
N_2	280	.080	286
N/O	280	.090	321
A/N/O	284	0.40	1,408
N_2	294	.200	680
N/O	340	.06	176
N_2	392	.050	128
A/N/O	400 (O_2)	.36	900
N/O	400 (O_2)	.290	725
A/N/O	446	.440	986
N/O	450 (O_2)	9.65	21,444
N/O	459	.402	876
A/N/O	491	.0731	149
A/N/O	589	30.26	51,380 *
O_2	680	.130	191
A/N/O	852	.110	129
N/O	891	.940	1,055
O_2	1,050	14.40	13,714 *
N/O	1,100	.37	336
A/N/O	1,114	.290	260
A/N/O	1,200	0.100	83
A/N/O	2,550	2.003	785
A/N/O	3,065	.500	163
N_2	5,840	.018	3

Table 5 (Continued)

Product	Production, T/day	Water Use, MGD	Water Use, gal/ton Product
N_2, H_2	179	.05	279
A/N/O, H_2	250	.089	356
N/O, H_2	984	.0376	38
A/N/O, H_2	5,870	100	17,035 *
H_2 (liq.)	16	.19	11,875 *
H_2, CO_2	289	.820	2,837
CO_2	85	1.42	16,705 *
CO_2	112	.0590	524
CO_2	200	.020	100
CO_2	200	.0082	41

* Once through cooling systems

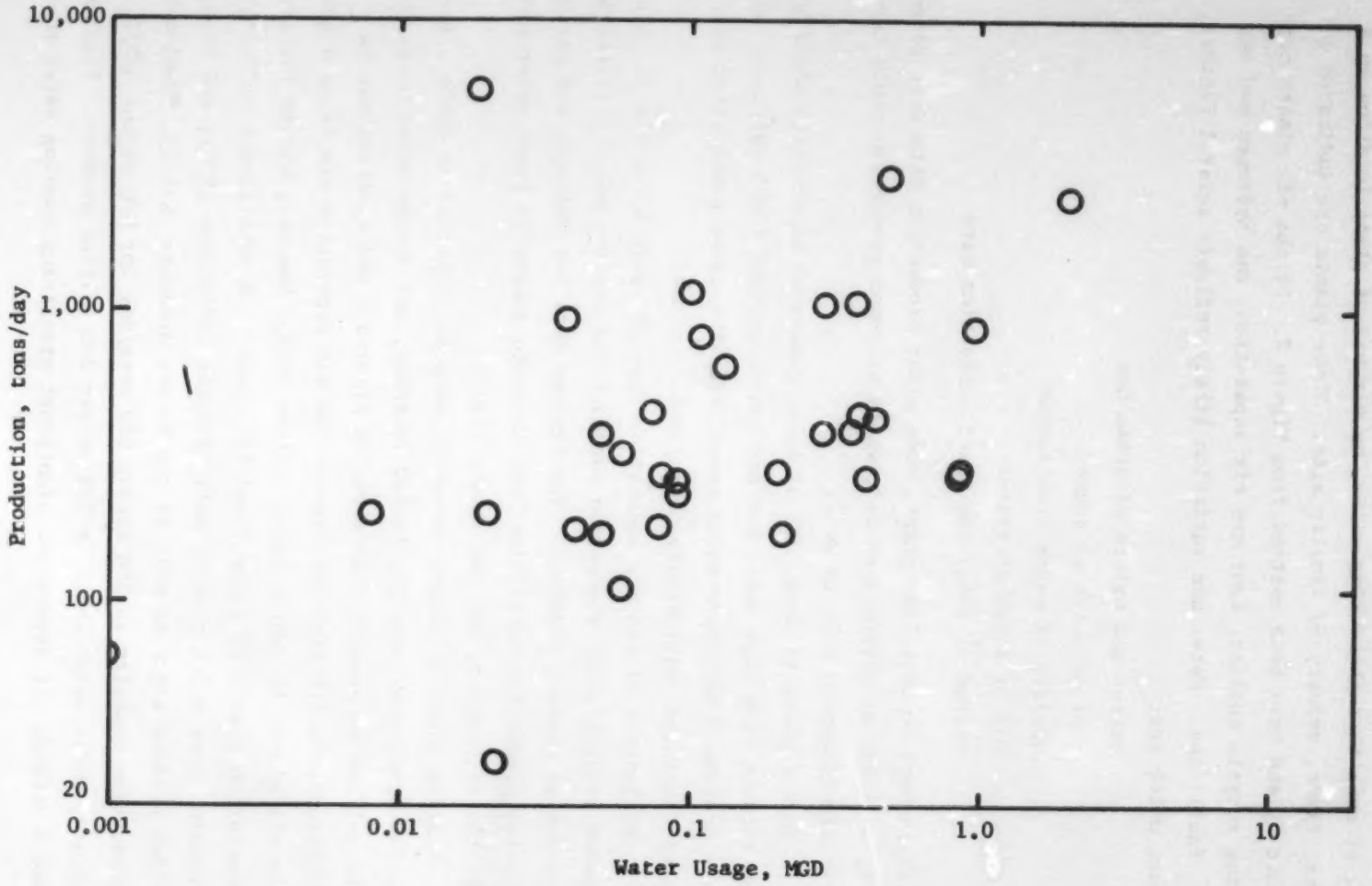

Figure 2. Comparison of Plant Production to Water Use

use of once through cooling water, by virture of plant location on a lake, river, estuary or similar site. These plants are indicated in Table 5, and have been omitted from Figure 2. Of the six plants not using recycle cooling, four are air separation, one hydrogen and one CO_2 facilities. Water use variation likely reflects several factors, among which are:

extent and nature of steam use
cost of water at source
quality of water from source
use of scrubber systems
method of reporting plant production data

With respect to this last point, some plant production data were given only in terms of oxygen produced, while nitrogen production could have been significantly high as well.

In one plant visited, use of steam generated electricity clearly contributed to a high water use per ton of product (1055 gal/ton). Even when cooling water represented essentially the total plant water use, rates fluctuate considerably from plant to plant.

Evaluation of the air separation data of Table 5 reveals no correlation between plant production capacity and cooling water utilization per ton of product produced. The limited data for hydrogen and carbon dioxide production facilities does indicate generally lower water use per ton of product, for the larger plants.

Among those 40 plants for which data are reported in Table 5 the median production capacity is 400 tons/day, and median water usage is 300 gal/ton of product. As shown in Figures 3 and 4, there was no difference in distribution between the air separation plants as a group, and all plants for which Table 5 lists data. However, within the air separation plants (Figures 5 and 6), there is a significant difference between those which produce only nitrogen and oxygen (N/O), and those which produce argon as well as the former products (A/N/O). Median production capacity is 200 versus 650 tons/day for N/O versus A/N/O plants, while water usage is 350 versus 200 gal/ton product. Figures 5 and 6 exclude air separation plants not practicing cooling water recycle,

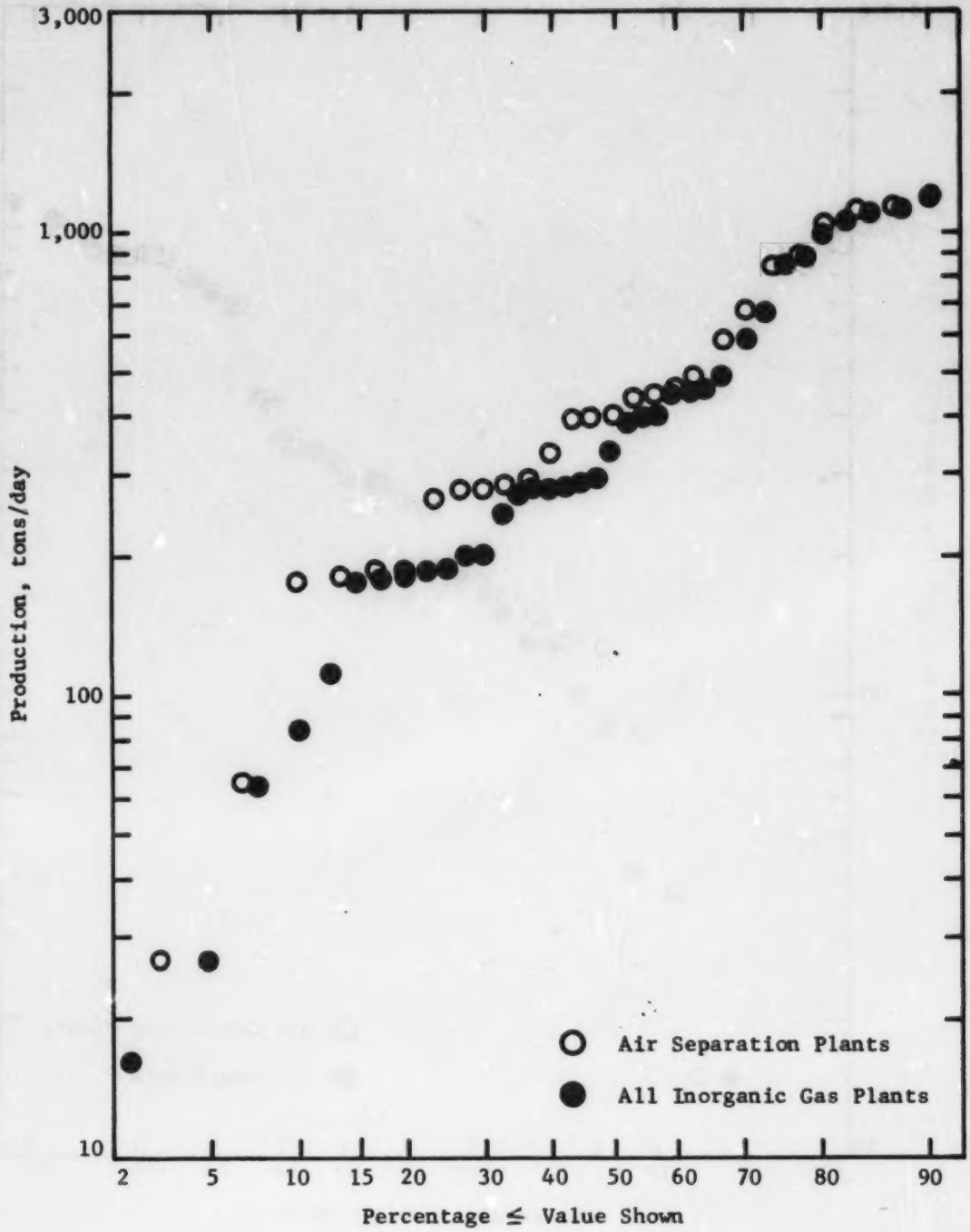

Figure 3. Distribution of Production for Gas Plants

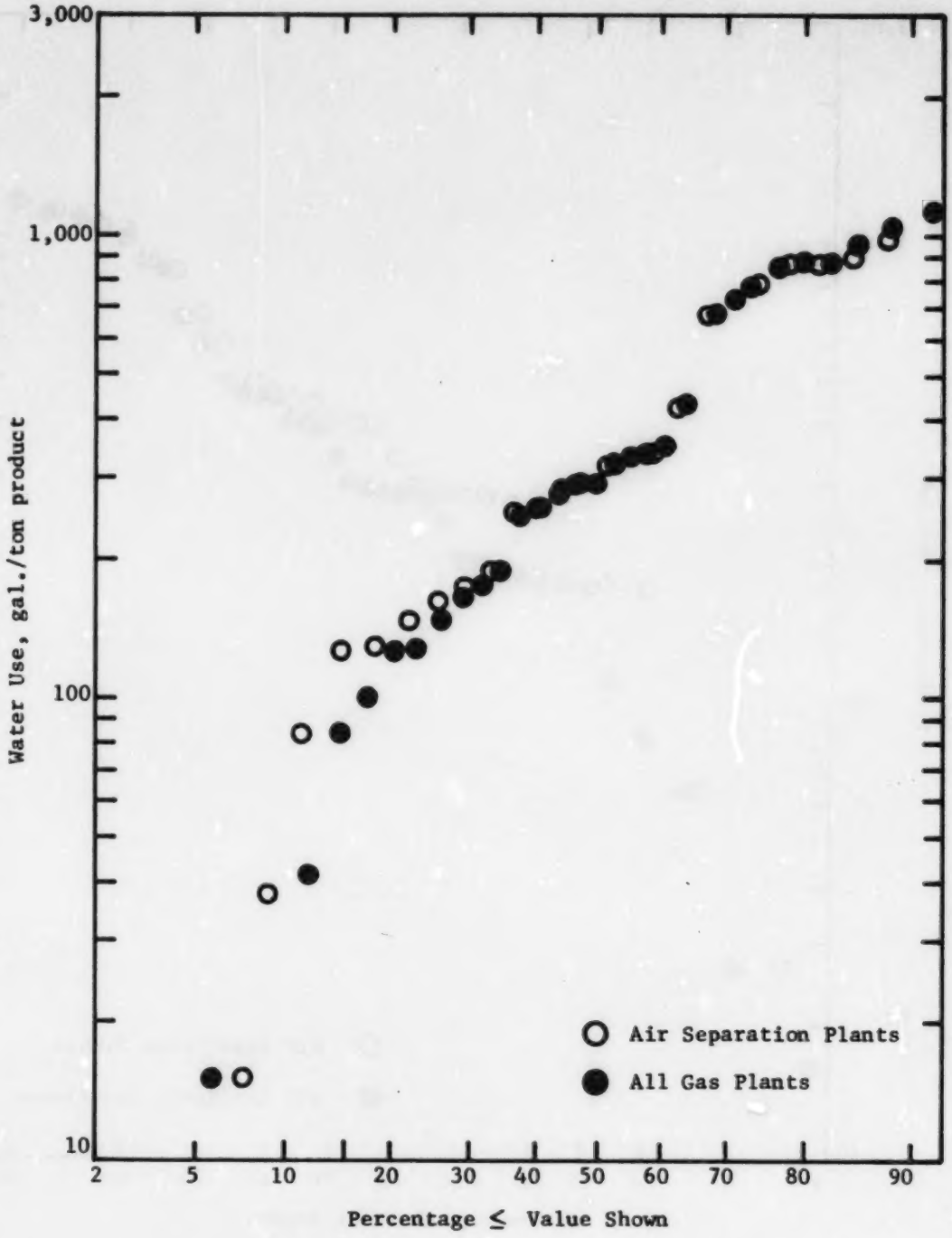

Figure 4. Distribution of Water Use for Gas Plants

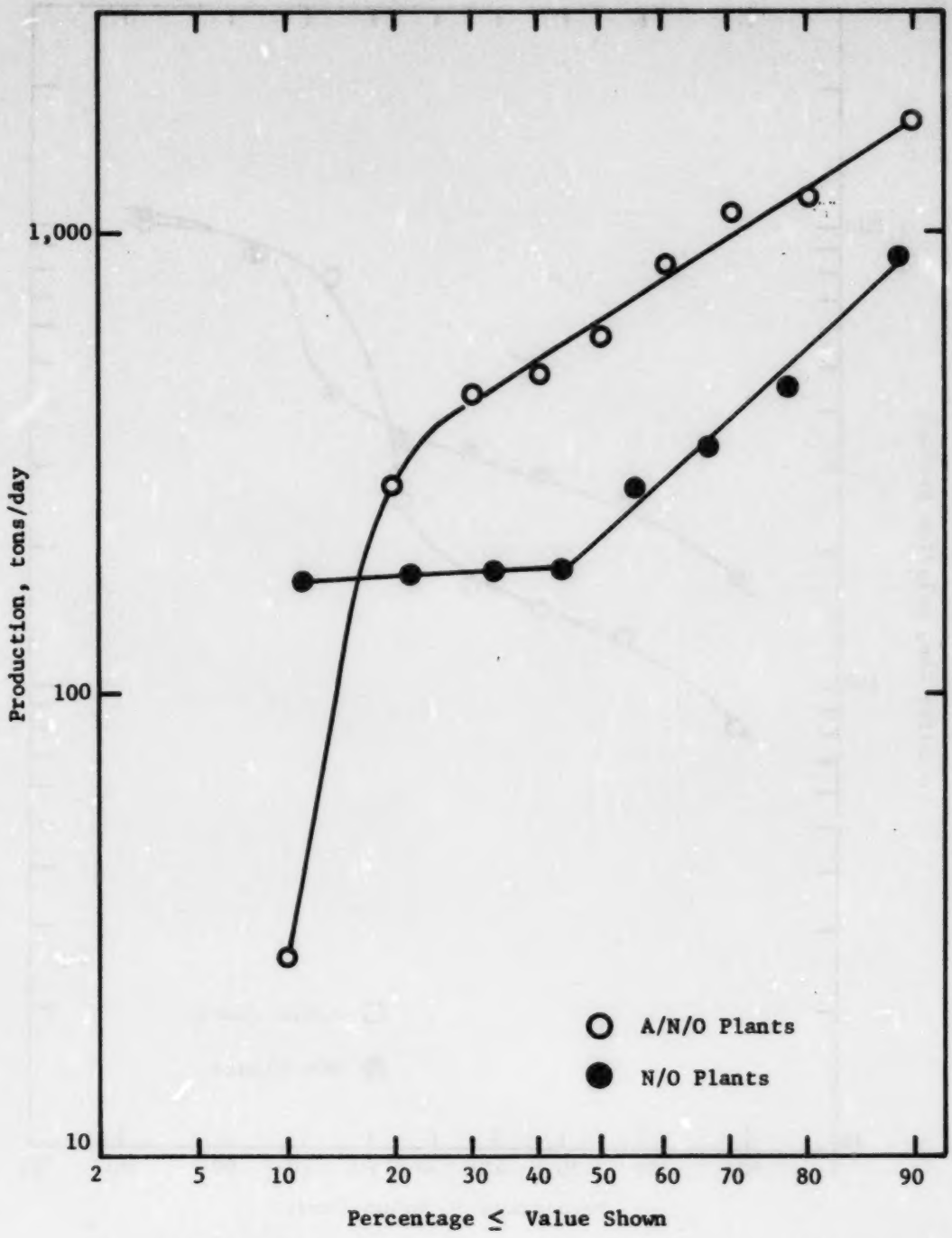

Figure 5. Distribution of Production for Air Separation Plants

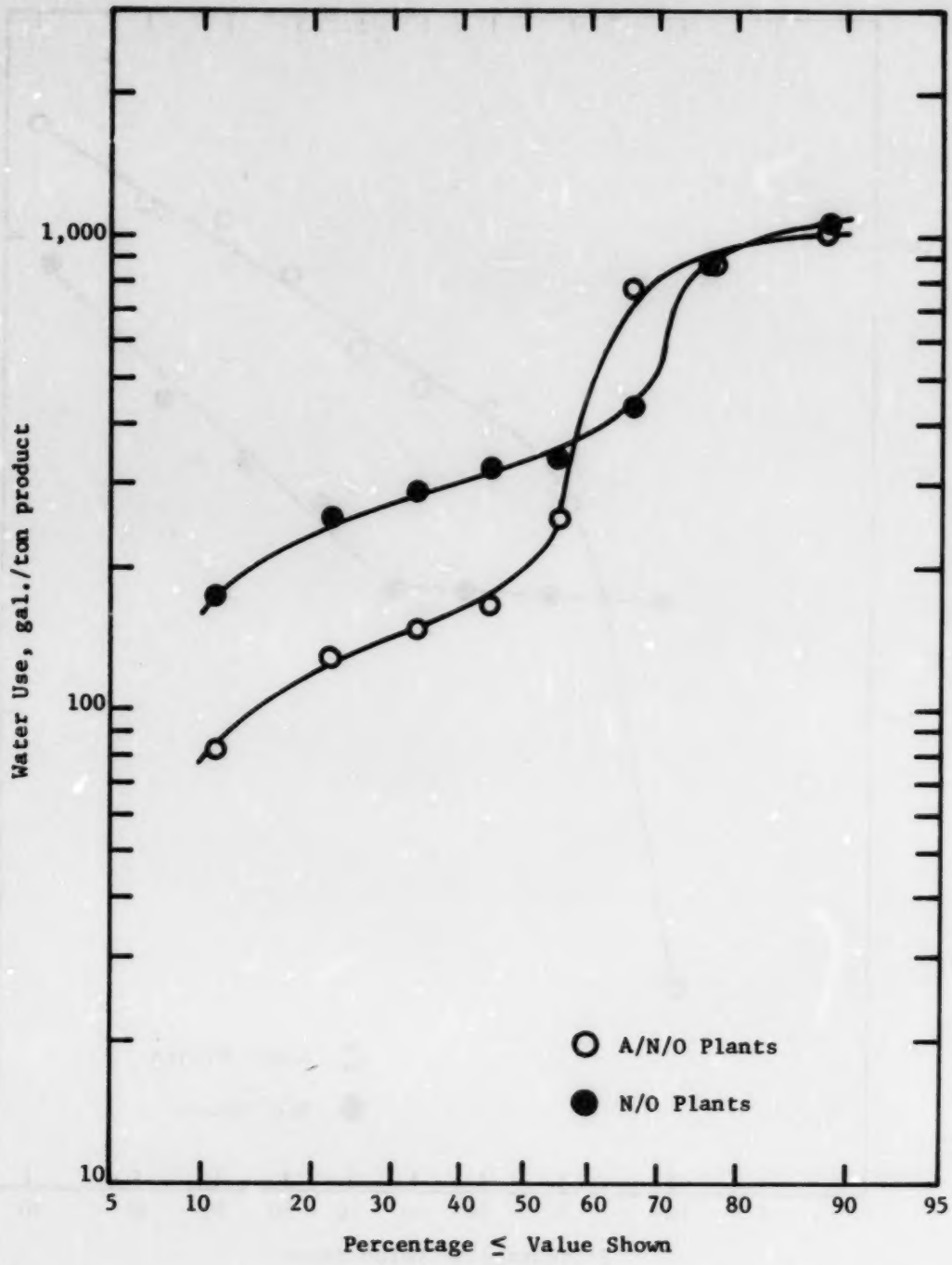

Figure 6. Water Use in Air Separation Plants

as well as plants which also produce either hydrogen or carbon dioxide, or for which only oxygen production data was reported.

It is unlikely that the larger production of the A/N/O plants, as compared to the N/O plants, is due solely to the production of argon. More likely, it is characteristic that an air separation plant designed to produce larger quantities of N/O would also incorporate an argon system as an adjunct. This reasoning, however, is not applicable to the water use data. N/O plants use more water per ton of product then A/N/O plants. This perhaps reflects less efficient cooling system design for the smaller (ie. N/O only) segment of the air separation industry.

Average water usage, based upon the data of Table 5 excluding once-through cooling systems are, for all plants, A/N/O and N/O respectively 491, 537 and 546 gal/ton product. Average values are thus more comparable then median values. The averages represent 9 A/N/O, 9 N/O and 31 total plants from Table 5. The remaining 9 plants either used once-through cooling or did not report total production tonnage.

Sources of Wastes

Sources of waste in industrial gas manufacturing plants are relatively few, and easy to identify. These are:

process condensate
cooling water discharge
boiler blowdown
boiler condensate
boiler (and occasionally cooling) water treatment discharge
plant wash down
scrubber solution dump
paint stripping solutions

In the air separation process, in-let gas upon compression and cooling produces a condensate waste. This water may be relatively clean in plants using the newer nonlubricated compressors. Older technology employs lubricated units, which contribute oil to the condensate. A few air separation plants use alkaline scrubbers for CO_2 removal after

air compression and the spent caustic constitutes a waste. Beyond these aspects, aqueous waste is not produced, as downstream cooling is condensate free and accomplished by closed systems. When CO_2 scrubbers are not used, all moisture, CO_2 and trace atmospheric organic contaminants are removed by thermally regenerated system (gel traps, alumina or reversing cryogenic heat exchangers). The deoxygenation process for argon purification may produce water containg nitrogen oxides, where ammonia is used as the reductant.

Cooling water character may be relatively unchanged for once through systems, except for temperature increase and possible chlorine addition at the intake. When cooling towers are employed, evaporative losses are often significant, and overall constituent concentrations are magnified by the factor employed to regulate the particular unit's blowdown rate (ie. number of recycles). Chemical additions to control corrosion and biological activity constitute contaminants in the blowdown, and this plus evaporative concentration dictate the nature of this waste stream.

Boiler operation can contribute to the waste stream in several respects. Steam condensate may be discharged relatively clean, or may contain volatile additives such as antiscaling amines. The boiler is blown down either periodically or continuously, and blowdown generally contains several additives. Boiler water pretreatment contributes solids where coagulation or softening is practiced. Ion exchange softening (generally with synthetic zeolites) produces waste brine regenerant solutions, which require disposal.

Plant wash down will reflect general plant housekeeping practices and could conceivably represent an oily waste depending upon the overall nature of equipment in use. Specific wastewaters also result from cleaning and stripping of paint from product gas cylinders. High lead wastes can be associated with such operations.

The only significant difference between air separation and carbon dioxide production lies in the nature of the raw CO_2 source. In one plant visited, raw CO_2 received from an adjacent petrochemical manufacturing operation contained roughly 1 lb. of condensate per lb. of

product CO_2. In addition to water, this condensate contained organic compounds, including glycols. When organics removal is not accomplished by condensation and bleed off or adsorptive processes, an oxidizing scrubber such as permanganate or dichromate may be used. These solutions may represent a disposal problem. Otherwise, compressor condensates, boiler blowdown and related wastes, and cooling tower blowdown considerations are similar to those of air separation units. Scrubber systems for CO_2 enrichment are normally regenerated, and typically represent a waste problem only if periodic dumping is required.

The major hydrogen production process, hydrocarbon reforming, has a water by-product condensate which should be essentially uncontaminated. The monoethanolamine scrubbing system is regenerated continuously and some water condensate is generated, supposedly uncontaminated although no substantive data were available. Other discharge sources are similar to those previously discussed for air separation and carbon dioxide facilities.

Hydrogen production by catalytic cracking of ammonia uses cooling water after the cracking process, and for cooling after compression of product. No specific wastewater information was available on hydrogen production by the partial oxidation of hydrocarbons with 95% oxygen. Since a mixture of gases is obtained, including CO, CO_2 and H_2O, scrubbing and condensation would be expected, with unit operations common to the reforming and ammonia cracking processes.

Quantity of Wastes

Wastewater volume data are tabulated in Table 6, on the basis of gallons per ton of product. These data were restricted to plants for which total discharge could be determined, and which did not use once through cooling water. Where possible total production data were used for computation. However, some production data were presented for oxygen only, as indicated in the Table. Another uncertainty in these data lies in whether or not the reported production is design capacity of the plant or actual average production. The former is suspected, on the basis of experience with those plants visited.

Table 6. Waste Volume per Ton of Product

Product	Production Rate	Discharge, Cal/T Product
A/N/O	284	35
A/N/O	284	357
A/N/O	321	62
A/N/O	400 (O_2)	300
A/N/O	446	538
A/N/O	852	48
A/N/O	2550	196
A/N/O	3065	82
N/O	270 (O_2)	70
N/O	280	54
N/O	284	56
N/O	284	35
N/O	340 (O_2)	21
N/O	400	35
N/O	459	544
N/O	891	169
N/O, H_2	1,100 (O_2)	78
N_2	280	43
N_2	294	75
N_2	392	51
N_2	5840	1
O_2	640	74
H_2	16	2875
H_2, N_2	179	112
H_2, CO_2	289	1211
CO_2	200	12

For 8 A/N/O plants, the average discharge was 202 gal/ton product, with values ranging from 35 to 538 gal/ton. Those 8 plants producing N/O only, had an average discharge of 123 gal/ton and a range of 21 to 544. A/N/O and N/O plants are thus comparable on this basis. Other gas plants generally fell within the same range, except for two hydrogen plants for which the water use was much higher. Figure 7 presents the cumulative distribution of discharges (gal/ton product) for A/N/O, N/O, and all plants. However, plants reporting oxygen data only were excluded. Median discharge for A/N/O and all plants was equal, at approximately 650 gal/ton. Discharge for the N/O plants was somewhat lower, at 450-550 gal/ton product. Based upon the limited amount of data for N/O facilities, this difference may not be real. Figure 6 indicated that the median water utilization for N/O plants was 350 gal/ton product, as compared to a median discharge of 450-550.

The average for all plants, except those reporting only partial production data, was 303 gal/ton product. For comparison, the average water intake volumes for all plants, A/N/O and N/O, respectively, were 491, 537 and 546 gal/ton. These values are tabulated below:

	All Plants	A/N/O Plants	N/O Plants
Average Inflow	491	537	[illegible]
Average Discharge	303	202	123
Percent Reduction	38.3	62.4	77.5

General analysis of water use data indicates that the major quantity of waste water results from cooling tower blowdown. Water balances reported suggest that evaporative losses are high, and that condensate volume in air separation plants is small relative to the cooling tower blowdown volume.

Character of Wastes

The nature of the waste stream is dictated by several factors. Essentially these are:

1. Specific in-plant treatment processes and/or actual

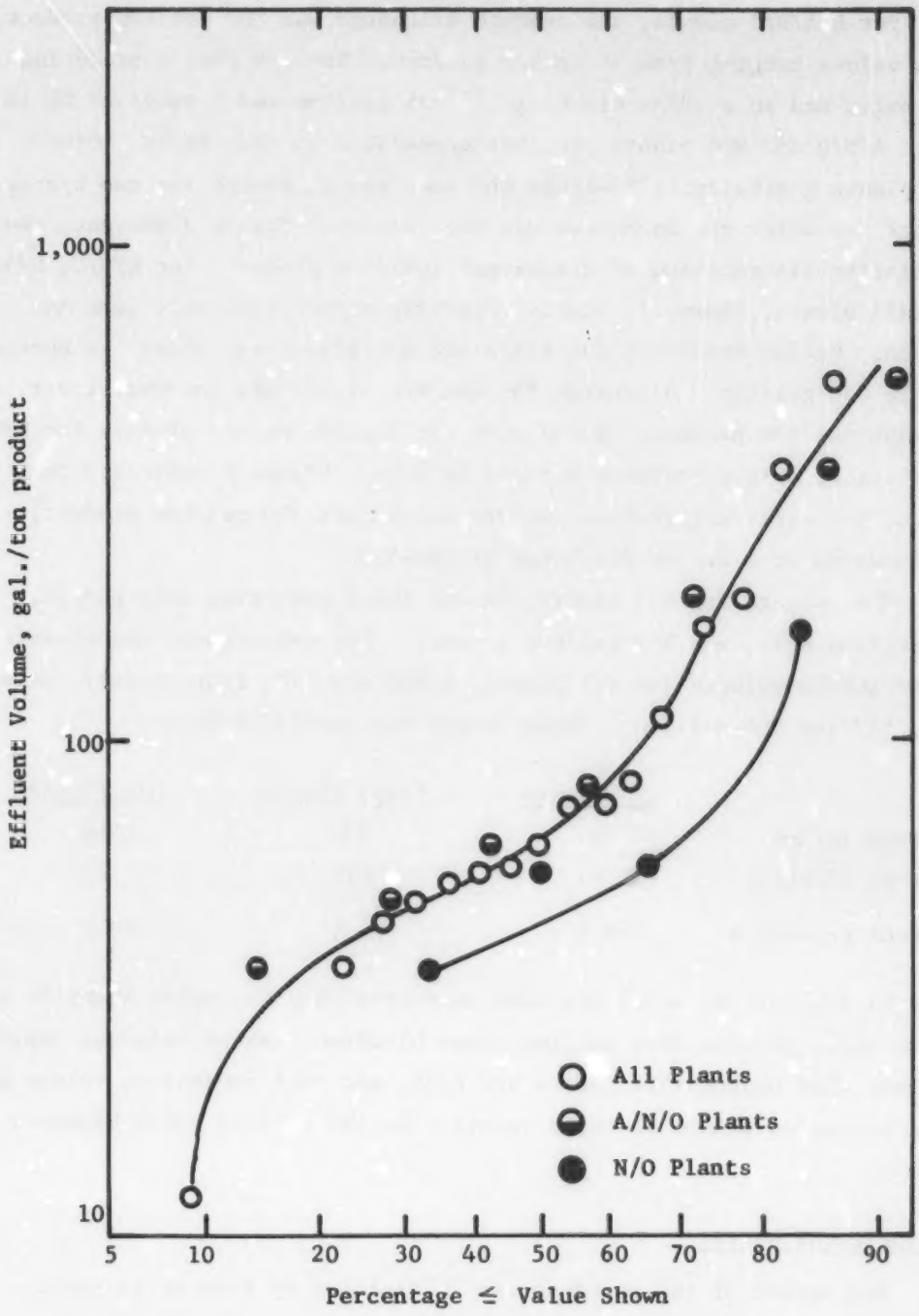

Figure 7. Distribution of Effluent Volumes for Gas Plants

manufacturing technology in use.

2. Direct addition of process wastes and condensates
3. Discharge of in-plant boiler water treatment wastes
4. Evaporative concentration of intake water constituents
5. Nature and quantity of cooling and boiler water additives
6. Auxilliary activities such as plant washdown and gas bottle paint stripping operations

These factors impact upon the chemical character of the waste discharge. In addition, since the bulk of discharge water results from cooling systems, elevated temperatures are also experienced.

Characterization of effluent nature by examination of permit applications proved to be difficult for several reasons. First, much reported data is based upon a single grab or single composite sample. Secondly, not all constituents are reported on all permit applications. In many cases, plant effluent data are given but no corresponding data are supplied for the intake water. In other cases, conversion of effluent concentrations to lbs/day and lbs/unit product based on values given for waste flow and production do not agree with those values reported in the permit application. Complicating this situation further is the fact that analytical data reported on influent and effluent concentrations of what would be expected to be conservative constituents (those not added or involved in chemical reactions leading to removal) do not show agreement among themselves, nor correlate with calculated concentration factors resulting from influent:effluent water ratios. Most likely several factors are involved, among which are poor estimates of flow, poor analytical precision, collection of influent and effluent samples under significantly different conditions, and insufficient numbers of samples to provide representative averages. Total mass balances were not obtained in most instances.

Based on influent:effluent water ratios for 30 plants, the mean discharge concentration factor was 4.5, with a range of 1.6 to 9.1. A comparison of this value with effluent:influent ratios for selected constituents is given for 19 plants in Table 7. Although there is a great deal of scatter in the concentration data, a general trend of

Table 7. Ratios of Effluent to Influent Concentrations

Product	Production ton/day	Water, in:out	Total Dissolved Solids	Sulfate	Chloride	Calcium	Sodium
A/N/O	3065	2.0	1.4	-	3.6	4.0	3.9
A/N/O	1114	7.0	0.69	-	-	-	-
A/N/O	852	3.4	2.9	4.0	-	-	-
A/N/O	400 (O_2)	3.0	1.8	1.3	2.8	2.5	2.1
A/N/O	321	3.9	5.8	8.0	0.95	-	-
N/O	981	6.2	6.9	-	-	-	-
N/O	340 (O_2)	8.6	-	2.8	2.0	-	2.9
N/O	280	4.5	2.9	2.7	2.9	2.7	-
N/O	270 (O_2)	4.5	1.9	6.2	2.6	-	3.6
N/O	-	5.1	4.8	20.0	2.3	-	3.1
N/O, H_2	1100 (O_2)	5.3	2.3	1.3	1.4	.74	3.8
N_2	5840	3.0	-	22.5	3.3	-	4.4
N_2	392	4.0	2.7	1.1	1.0	1.4	3.5
N_2	294	9.1	3.9	8.9	4.3	4.4	5.9
N_2, H_2	179	2.5	2.5	-	-	-	-
O_2	640	4.0	3.4	2.3	2.2	2.2	-
H_2	16	4.9	5.7	12.4	5.2	5.2	5.2
H_2, CO_2	289	2.5	5.1	1.0	13	1.1	2.0
CO_2	200	8.3	1.9	6.3	1.7	36.5	-
Average		4.8	3.3	6.7	3.3	6.1	3.7

increasing concentration with increasing water (influent:effluent) ratios is observed. A comparison of the averages of Table 7 shows comparable values for dissolved solids, chloride and sodium, all of which are close to the water discharge ratio. Except for the one large concentration factor of 36.5 reported for calcium at one carbon dioxide plant, the calcium ratio (2.7) is also comparable. The sulfate concentration factor is high, as are many of the individual values reported. This likely results from sulfuric acid addition to recycled cooling waters, for pH control. Sodium values would be expected to reflect a similar increase to chloride and this is evident from the data. In general, the concentration factors are of the same order of magnitude, indicating that the primary contribution to increased effluent concentrations is evaporation of cooling water, and where appropriate, consumptive use of steam.

Data for nitrogen and phosphorus forms usually did not show similar concentration factors. Usually, little or no change was evident, implying that removal of these elements might be occurring in cooling systems through biological action.

BOD and COD discharges are presented in Table 8 for 15 plants. Significant increases in BOD and COD values are apparent for several of these plants. There is no correlation between the water use (influent: effluent) ratio and either BOD or COD concentration factors, for individual plants. However, the average concentration factors for BOD and COD, at 6.9 and 7.0 respectively, are very close. Both are higher then the average water use ratio of 4.8, indicating addition of organic waste in the gas processing. This likely reflects organic condensate blowdown, and oil and grease leakage from compressors, or organic additives in the cooling water system. Table 9 presents BOD and COD data on the basis of production. BOD discharge for the air separation plants, with the exception of the one plant also producing carbon dioxide, falls within the range of 0.0037 to 0.0156 lbs. per ton product. The average BOD for all plants for which sufficient data was available is 0.0426 lbs. per ton product. Average COD discharge is much higher at 0.2481 lbs/ton, although if the extremely high discharge

Table 8. BOD and COD Concentrations and Concentration Ratios

Product	Production, ton/day	Water in:out	BOD			COD, mg/l		
			Influent*	Effluent*	Ratio	Influent*	Effluent*	Ratio
A/N/O	3065	2.0	0	10	-	17	60	3.5
A/N/O	1114	7.0	0	5	-	31	20	0.6
A/N/O	400 (O_2)	3.0	1.4	1.6	1.1	32.3	62.2	1.9
A/N/O	321	3.9	-	-	-	7	214	30.6
N/O	891	6.2	2	3	1.5	2	40	20.0
N/O	280	4.5	5	35	7.0	7	49	7.0
N/O	270 (O_2)	4.5	1	1	1.0	1	0	-
N/O	-	5.1	2	1	0.5	-	-	-
N/O, H_2	1100 (O_2)	0	0	7	-	8	18	2.3
N_2	392	4.0	1.4	24	17.1	0	79	-
N_2	294	9.1	2	12	6.0	5	190	38.0
N_2, CO_2	289	2.3	0.8	10	12.5	12	40	3.3
N_2, H_2	179	2.5	2	4	2.0	2	16	8.0
CO_2	200	8.3	-	-	-	.4	16	40.0
H_2	16	4.9	0	8	-	0	70	-
Average		4.8	1.4	9.4	6.9	8.9	62.4	7.0

* Expressed in mg/l.

Table 9. Mass Discharge of BOD and COD per Ton Product

Product	Production tons/day	BOD, lbs x 10^3/ton product	COD, lbs x 10^3/ton product
A/N/O	3065	6.8	40.8
A/N/O	321	-	111.2
N/O	891	4.2	56.2
N/O	280	15.6	21.9
N_2	392	10.2	33.6
N_2	294	7.5	118.6
N_2, H_2	179	3.7	14.9
N_2, CO_2	289	101.0	404.0
CO_2	200	-	1.3
H_2	16	191.8	1,678.4
Average, lbs/ton		42.6×10^{-3}	248.1×10^{-3}

of the hydrogen plant is omitted this average drops to 0.0892 lbs/ton.

Contaminants of significance, based on consideration of additives to the water passing through the plant rather than increases due to evaporation, seem to be sulfate from sulfuric acid addition, chloride from brine discharge, and chromium, zinc and occasionally iron and copper from corrosion inhibitor and biocide treatment of cooling water. Nonmetallic organic biocide additives contribute to COD analysis values. Oil and grease are present in some effluents and reflect plant washdown practices or use of lubricated compressors. Data regarding these parameters are summarized in Tables 10 through 12.

In Table 10, chromium data are reported only for those plants implying use of chromium by their permit applications. Some plants showed no increase in chromium values between influent and effluent. Others reported no values for chromium. In some cases information indicated discontinuation of chromate use. While effluent values range from less then 1 to 23 mg/l, discharge per ton of product values vary over 3 orders of magnitude, reflecting the wider range of water discharge per ton of product (Table 5).

Similar results are demonstrated for effluent zinc values in Table 11. Concentrations vary over an order of magnitude while discharge per ton of product varies over 3 orders of magnitude. Relatively little data were available for oil and grease discharges, as shown in Table 12.

A consideration of the purpose of chromium or zinc addition to cooling waters, which is for corrosion and biological control, suggests that from an economic point addition would be based upon maintaining an effective concentration in the cooling water, and that effluent concentration should be more consistent then mass discharge per ton of product. Therefore, for these two parameters there appears to be little merit in considering their discharge on a mass per ton of product basis, since effluent volume shows no such correlation.

Tables 10, 11 and 12 indicate that one hydrogen plant (16 ton/day) was consistently highest in pollutant discharge per ton of product, and much higher then any other plant for which data were available. The

Table 10. Selected Values of Chromium Discharge

Product	Production, tons/day	Water Conc. Factor	Conc. in, mg/l	Conc. out, mg/l	Chromium Conc. Ratio	Discharge, lbs x 10^3/ton prod.
A/N/O	3065	2.0	.01	.65	65	0.4
A/N/O	2550	4.0	-	4.0	-	6.5
A/N/O	446	1.8	.2	11.5	58	51.6
N/O	340 (O_2)	8.6	0.05	2.7	-	0.5
N/O	270 (O_2)	4.5	0.05	11.0	-	6.5
N_2	392	4.0	0	22.6	-	4.8
N_2	294	9.1	0.05	4.0	8	2.5
O_2	640	4.0	0.05	1.90	38	1.2
H_2	16	4.9	0	8.1	-	194.2
CO_2	200	1.0	.2	3.4	17	1.1
CO_2	200	8.3	.2	3.0	15	0.3
Average		4.7	0.07	6.6	94.3	24.5 x 10^{-3}

Table 11. Selected Values of Zinc Discharge

Product	Production	Water Conc. Factor	Conc. in, mg/l	Conc. out, mg/l	Zinc Conc. Ratio	Discharge lbs x 10^3/ton prod.
A/N/O	3065	2.0	.01	.51	51	0.3
A/N/O	446	1.8	0.1	3.4	34	15.2
A/N/O	400 (O_2)	3.0	.067	4.77	71	11.9
N/O	340 (O_2)	8.6	.050	.35	7	0.06
N/O	284	8.0	-	1.0	-	0.3
N/O	270 (O_2)	4.5	.050	10.0	200	5.9
N/O	-	10.0	.03	5.3	177	-
N/O	-	5.1	.05	2.0	40	-
N_2	5840	3.0	.050	1.20	24	0.01
N_2	392	4.0	.004	12.5	3125	2.7
N_2	294	9.1	.03	1.9	63	1.2
N_2	280	6.0	.05	2.9	58	1.1
H_2	16	4.9	0	11.8	-	282.9
H_2, CO_2	289	2.3	.05	3.5	70	35.4
CO_2	200	1.0	.02	1.3	65	4.4
CO_2	200	8.3	.3	2.1	7	0.2
Average		4.5	0.06	4.03	67.2	25.8 x 10^{-3}

Table 12. Summary of Oil and Grease Discharge Data

Product	Production, tons/day	Conc. in, mg/l	Conc. out, mg/l	Discharge lbs x 10^{3}/ton prod.
A/N/O	3065	0	11	7.5
A/N/O	2550	-	15	24.5
A/N/O	289	0	5.0	50.5
N/O	284	-	30	14.1
N/O	284	-	30	8.8
N/O	280	-	20	8.9
N_2	392	0	15.8	3.4
N_2	280	0	19	7.4
H_2	16	0	10	240.0
Average		-	17.3	40.6 x 10^{-3}

values for chromium, zinc, and oil and grease for this plant were 0.1942, 0.2829, and 0.240 lbs/ton while the respective averages for all other plants (excluding that hydrogen plant) were 0.0075, 0.0060 and 0.0157 lbs/ton. Thus, this single plant greatly influenced the averages presented in Tables 10 through 12.

Effluent pH values were always in the range of 6.0 to 9.0. In part, this reflects the fact that most discharge water results from cooling water systems which are controlled to maintain proper pH. Batch dumping of alkaline scrubber water would significantly alter effluent pH. However, where used in plants visited, the concentrated caustic solutions were contracted out separately for disposal.

Table 13 summarizes the reported temperature changes between influent and effluent waters in terms of average summer and winter values. These data are for both once through and cooling tower systems. For 31 plants, the mean temperature changes were 14.0°F for the summer and 14.5°F for the winter. Ranges of temperature change were -5 to 41°F for summer and -5 to 49°F for the winter.

Table 13. Summary of Temperature Information

Product	Production, tons/day	Inflow Temp., °F Summer	Inflow Temp., °F Winter	Outflow Temp., °F Summer	Outflow Temp., °F Winter
A/N/O	5870	65	40	82	50
A/N/O	3065	80	80	87	78
A/N/O	2550	78	75	90	85
A/N/O	1114	65	44	106	93
A/N/O	852	75	55	75	55
A/N/O	589	80	40	82	42
A/N/O	446	64	55	86	74
A/N/O	400 (O_2)	65	55	85	75
A/N/O	321	70	40	80	60
A/N/O	287	85	70	90	80
A/N/O	284	84	75	90	82
N/O	1050 (O_2)	87	77	98	83
N/O	871	70	40	80	45
N/O	459	85	70	90	80
N/O	400	70	65	65	60
N/O	340 (O_2)	73	45	83	63
N/O	284	85	70	90	81
N/O	284	74	71	90	84
N/O	280	85	70	90	81
N/O	270 (O_2)	60	40	85	70

Table 13. Summary of Temperature Information

Product	Production, tons/day	Inflow Temp., °F Summer	Inflow Temp., °F Winter	Outflow Temp., °F Summer	Outflow Temp., °F Winter
A/N/O	5870	65	40	82	50
A/N/O	3065	80	80	87	78
A/N/O	2550	78	75	90	85
A/N/O	1114	65	44	106	93
A/N/O	852	75	55	75	55
A/N/O	589	80	40	82	42
A/N/O	446	64	55	86	74
A/N/O	400 (O_2)	65	55	85	75
A/N/O	321	70	40	80	60
A/N/O	287	85	70	90	80
A/N/O	284	84	75	90	82
N/O	1050 (O_2)	87	77	98	83
N/O	871	70	40	80	45
N/O	459	85	70	90	80
N/O	400	70	65	65	60
N/O	340 (O_2)	73	45	83	63
N/O	284	85	70	90	81
N/O	284	74	71	90	84
N/O	280	85	70	90	81
N/O	270 (O_2)	60	40	85	70

Table 13.(Continued)

Product	Production, tons/day	Inflow Temp., °F Summer	Inflow Temp., °F Winter	Outflow Temp., °F Summer	Outflow Temp., °F Winter
O_2	640	75	40	85	50
O_2	450	85	55	95	66
N_2	5840	75	60	85	70
N_2	392	70	50	90	80
N_2	294	70	50	90	80
N_2	280	84	70	90	80
N/O, H_2	1100 (O_2)	64	40	85	70
N_2, H_2	179	70	50	106	90
H_2	16	77	77	85	82
H_2, CO_2	289	77	77	102	94
CO_2	85	63	52	94	86

VII. CONTROL AND TREATMENT TECHNOLOGY

There are two approaches to handling waste problems in the inorganic gas industry. In-plant control to eliminate the waste characteristics of concern, and treatment of the waste stream to reduce the contaminant to acceptable levels. Within the air separation industry, in-plant controls are capable of complete elimination of the discharge of oil and grease and caustic wastes, as well as chromium and zinc associated with cooling tower blowdown. Current manufacturing technology and cooling tower treatment practice have demonstrated that air separation plants can be pollution free, exclusive of their concentrating of inlet water constituents.

Modern plants use nonlubricated compressors, yielding pure water condensate. Carbon dioxide removal is accomplished by reversing heat exchangers, silica traps or molecular sieves, all of which are thermally regenerated and exhaust original air constituents back to the atmosphere. Chromate and zinc additives to cooling water systems can be and in many plants have been replaced by other acceptable treatment chemicals. Any problem beyond this aspect is not specific to this industry as such, but a problem of cooling water blowdown in general. Primarily the solution relates to use of acceptable additives for corrosion inhibition and biological control, and discharge water of acceptable temperature differential relative to the receiving system.

Where steam systems are employed, water pretreatment will result in periodic brine or sludge discharge. Again this is a problem not unique to the inorganic gas industry. One solution is to use electric power from an off-site source. Under these circumstances, air separation plants require boiler systems only for backup purposes.

Existing plants utilizing older technology must apply oil removal techniques to the compressor condensates. Many plants have already taken this measure. Treatment ranges from simple catch tanks with surface skimmers and submerged outlets, to systems with emulsion breakers, skimmers and activated carbon clean-up. The technology and costs of

these systems are well established (2). Caustic scrubber systems are clearly outmoded and should be replaced by more modern CO_2 removal systems. The alternative is to dispose of the waste caustic by contract, as has been implemented by several plants.

Exclusive of those plants processing crude hydrogen or CO_2 from adjacent petrochemical facilities, where condensible organics represent a significant organic waste, hydrogen and CO_2 plants are analogous to the air separation plants in their waste generation and control considerations. Cooling tower blowdown, boiler blowdown and boiler water treatment wastes are the principal waste streams. Carbon dioxide removal and recovery systems, when properly designed and operated, have no liquid wastes as they are closed cycle regenerative systems exclusive of cooling water and condensate. Lubricated compressor systems are subject to the same considerations as air separation units, relative to oil and grease.

For plants processing raw gas streams, location adjacent to large petrochemical plants generally affords access to treatment units designed to handle the complex petrochemical waste. Contracting of condensate wastes to these adjacent facilities is in practice at several plants. One plant currently receiving bulk H_2 for bottling will in the future receive a raw H_2 stream. Clean-up is designed for the gas stream by activated carbon with thermal regeneration and atmospheric venting.

VIII. ACKNOWLEDGEMENTS

The cooperation of E. Martin and D. Becker of the Effluent Guidelines Division, and personnel of the regional offices of the Environmental Protection Agency, greatly assisted the performance of this study.

IX. REFERENCES

1. Shreve, R. N., Chemical Process Industries, 3rd. Ed., McGraw-Hill Book Co., N.Y.

2. Patterson, J. W. and R. A. Minear, "Wastewater Treatment Technology," 2nd Ed., State of Illinois Institute for Environmental Quality Report IIEQ 73-1, February, 1973.